

## Hair Dye Composition

BACKGROUND OF THE INVENTION

## 1. Field of the Invention

5 The present invention relates to a hair dye composition having excellent dyeing power, being capable of imparting a wide range of colors to the hair without losing their vividness, and showing less color fade over time.

## 2. Background Art

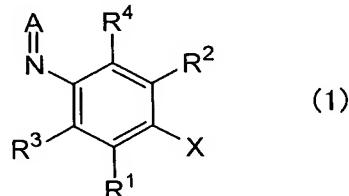
10 Hair dyes can be classified by a dye to be used therefor, or by whether they have bleaching action of melanin or not. Typical examples include a two-part permanent hair dye composed of a first part containing an alkali agent, an oxidation dye and optionally a direct dye such as a nitro dye and a second part containing an oxidizing agent; and a one-part semi-permanent hair dye containing an organic acid or an alkali agent, and an acid dye, basic dye or direct dye such as a nitro dye.

15 The above-described permanent hair dye is however accompanied by the drawback that the color tone imparted by an oxidation dye is not so vivid. Use of a nitro dye or cationic dye for a two-component hair dye containing an oxidizing agent has been attempted in order to produce various color tones (refer to, for example, Japanese Patent 20 Laid-Open Nos. 271435/1994 and 2001-261535). A hair dye

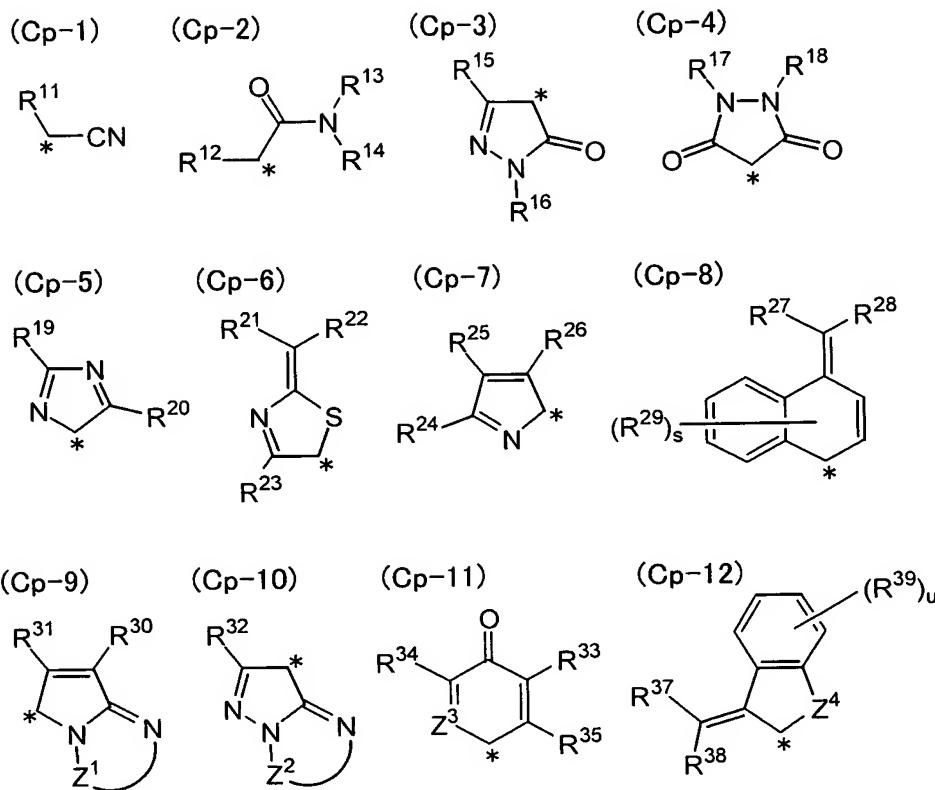
added with a nitro dye develops a vivid color just after  
 dyeing, but color fades away remarkably over time and tends  
 to be dull. Use of a cationic dye, on the other hand,  
 involves such problems that it is easily decomposed when  
 5 mixed with a peroxide serving as an oxidizing agent and it  
 cannot readily be used in combination with an anionic  
 polymer.

SUMMARY OF THE INVENTION

10 An object of the present invention is to provide a  
 hair dye composition comprising a dissociative direct dye  
 represented by the following formula (1):



15 wherein,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  each independently represents a  
 hydrogen atom or a substituent,  $X$  represents a hydroxyl  
 group or  $-NHSO_2R^5$ , in which  $R^5$  represents an alkyl, aryl or  
 heterocyclic group, and  $A$  represents a group represented by  
 any one of the below-described formulas (Cp-1) through (Cp-  
 12) with the proviso that the above-described groups may  
 20 have one or more substituents:



(in formulas (Cp-1) through (Cp-12), \* is a position  
bonding to the nitrogen atom in formula (1),

5 in formula (Cp-1),  $\text{R}^{11}$  represents a cyano group, acyl  
group, aryl group, heterocyclic group or a group  
 $-\text{C}(\text{R}^{101})=\text{C}(\text{R}^{102})-\text{R}^{103}$ , in which  $\text{R}^{101}$ ,  $\text{R}^{102}$  and  $\text{R}^{103}$  each  
independently represents a hydrogen atom or a substituent  
with the proviso that at least one of  $\text{R}^{102}$  and  $\text{R}^{103}$  is an  
electron attractive group having a Hammett  $\sigma_p$  value of 0.1  
10 or greater,

in formula (Cp-2),  $\text{R}^{12}$  represents a cyano,  
alkoxycarbonyl, carbamoyl, aryl or heterocyclic group, and  
 $\text{R}^{13}$  and  $\text{R}^{14}$  each independently represents a hydrogen atom or  
an alkyl, aryl or heterocyclic group,

in formula (Cp-3),  $R^{15}$  represents a hydrogen atom or an alkyl, aryl, heterocyclic, amino, alkylamino, arylamino, heterocyclic amino, alkoxy, acylamino, alkoxy carbonylamino, ureido, alkoxy carbonyl, carbamoyl or cyano group, and  $R^{16}$  represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

5 in formula (Cp-4),  $R^{17}$  and  $R^{18}$  each independently represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

10 in formula (Cp-5),  $R^{19}$  and  $R^{20}$  each independently represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

15 in formula (Cp-6),  $R^{21}$  and  $R^{22}$  each independently represents a cyano, carbamoyl, alkoxy carbonyl, alkylsulfonyl or arylsulfonyl group, and  $R^{23}$  represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

in formula (Cp-7),  $R^{24}$ ,  $R^{25}$  and  $R^{26}$  each independently represents a hydrogen atom or a substituent,

20 in formula (Cp-8),  $R^{27}$  and  $R^{28}$  each independently represents a cyano, carbamoyl, alkoxy carbonyl, alkylsulfonyl or arylsulfonyl group,  $R^{29}$  represents a substituent, and  $s$  stands for an integer of from 0 to 6,

25 in formula (Cp-9),  $R^{30}$  and  $R^{31}$  each independently represents a hydrogen atom or a substituent, and  $Z^1$  represents an atomic group necessary for the formation of a

6-membered ring together with N-C=N,

in formula (Cp-10), R<sup>32</sup> represents a hydrogen atom or a substituent, and Z<sup>2</sup> represents an atomic group necessary for the formation of a 6-membered ring together with N-C=N,

5 in formula (Cp-11), R<sup>33</sup>, R<sup>34</sup> and R<sup>35</sup> each independently represents a hydrogen atom or a substituent, Z<sup>3</sup> represents a nitrogen atom or -C(R<sup>36</sup>)=, and R<sup>36</sup> represents a hydrogen atom or a substituent, with the proviso that when Z<sup>3</sup> represents -C(R<sup>36</sup>)=, R<sup>34</sup> and R<sup>36</sup> may be coupled to form a 5-membered or 6-membered ring, and

10 in formula (Cp-12), R<sup>37</sup> and R<sup>38</sup> each independently represents a cyano, carbamoyl, alkoxy carbonyl, alkylsulfonyl or arylsulfonyl group, R<sup>39</sup> represents a hydrogen atom or a substituent, u stands for an integer of 15 from 0 to 4 and Z<sub>4</sub> represents -SO<sub>2</sub>- or -SO-), or salt thereof.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a hair dye 20 composition capable of dyeing the hair strongly into a vivid color tone without causing decomposition of the dye during the dyeing process, and exhibiting an excellent resistance against sunlight, hair washing, perspiration, friction and heat, having a high stability against an alkali agent and an oxidizing agent, having high dyeing 25

properties, and not fading away easily even after passage of time; and a hair dyeing method using the composition.

The dissociative direct dye of formula (1) used in the present invention has a phenolic hydroxyl group or a sulfonamide group  $-\text{NHSO}_2\text{R}^5$ . At a certain pH or greater, 5 proton dissociation occurs in the dye, which causes a change in color hue, thereby imparting a desired color hue to the hair. The dissociative direct dye (1) preferably does not contain, in the molecule thereof, a group which 10 dissociates at a neutral pH such as carboxyl group, sulfo group or quaternary ammonium group.

In formula (1), examples of the substituent represented by  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , or  $\text{R}^4$  include halogen atoms, alkyl groups, alkenyl groups, alkynyl groups, aryl groups, 15 heterocyclic groups, a cyano group, a hydroxy group, a nitro group, a carboxyl group, alkoxy groups, aryloxy groups, silyloxy groups, heterocyclic oxy groups, acyloxy groups, carbamoyloxy groups, alkoxy carbonyloxy groups, aryloxycarbonyloxy groups, an amino group, alkylamino groups, arylamino groups, heterocyclic amino groups, 20 acylamino groups, ureido groups, alkoxy carbonylamino groups, aryloxycarbonylamino groups, sulfamoylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups, a mercapto group, alkylthio groups, arylthio groups, 25 heterocyclic thio groups, sulfamoyl groups, a sulfo group,

alkylsulfinyl groups, arylsulfinyl groups, alkylsulfonyl groups, arylsulfonyl groups, acyl groups, alkoxy carbonyl groups, aryloxycarbonyl groups, carbamoyl groups, arylazo groups, heterocyclic azo groups, phosphino groups, 5 phosphinyl groups, phosphinyloxy groups, phosphinylamino groups and silyl groups. When these substituents are further substitutable, they may have one or more substituents.

10 Specific examples of the above-described substituents (including the case where they are substituted further) will next be described.

The halogen atoms include fluorine, chlorine, bromine and iodine atoms.

15 The alkyl groups include linear, branched or cyclic C<sub>1-10</sub>, preferably C<sub>1-6</sub> alkyl groups such as methyl, ethyl, n-propyl, isopropyl, t-butyl, n-octyl, 2-chloroethyl, 2-cyanoethyl, 2-ethylhexyl, cyclopropyl and cyclopentyl.

20 The alkenyl groups include linear, branched or cyclic C<sub>2-10</sub>, preferably C<sub>2-6</sub> alkenyl groups such as vinyl, allyl, prenyl and cyclopenten-1-yl.

The alkynyl groups include C<sub>2-10</sub>, preferably C<sub>2-6</sub> alkynyl groups such as ethynyl and propargyl.

25 The aryl groups include C<sub>6-12</sub>, preferably C<sub>6-8</sub> aryl groups such as phenyl, p-tolyl, naphthyl, 3-chlorophenyl and 2-aminophenyl.

The heterocyclic groups include aromatic or nonaromatic, monovalent C<sub>1-12</sub>, preferably C<sub>2-6</sub> groups obtained by removing one hydrogen atom from 5- or 6-membered heterocyclic compounds, such as 1-pyrazolyl, 1-imidazolyl, 2-furyl, 2-thienyl, 2-thiazolyl, benzothiazol-2-yl, isothiazol-5-yl, benzoisothiazol-7-yl, oxazol-2-yl, benzoxazol-2-yl, 1,2,4-thiadiazol-5-yl, 1,3,4-thiadiazol-2-yl, 1,2,4-oxadiazol-5-yl, 1,3,4-oxadiazol-2-yl, 1,2,4-triazol-3-yl, 4-pyridyl, 3-pyridyl, 4-pyrimidinyl and quinazolin-4-yl.

The alkoxy groups include linear, branched or cyclic, C<sub>1-10</sub>, preferably C<sub>1-6</sub> alkoxy groups such as methoxy, ethoxy, isopropoxy, t-butoxy, cyclopentyloxy, 2-buten-1-yloxy and 2-methoxyethoxy.

The aryloxy groups include C<sub>6-12</sub>, preferably C<sub>6-8</sub> aryloxy groups such as phenoxy, 2-methylphenoxy, 4-t-butylphenoxy and 3-nitrophenoxy.

The silyloxy groups include C<sub>3-10</sub>, preferably C<sub>3-6</sub> silyloxy groups such as trimethylsilyloxy and t-butyldimethylsilyloxy.

The heterocyclic oxy groups include C<sub>1-12</sub>, preferably C<sub>2-6</sub> heterocyclic oxy groups such as 1-phenyltetrazol-5-oxy and 2-tetrahydropyranloxy.

The acyloxy groups include C<sub>1-12</sub>, preferably C<sub>1-8</sub> acyloxy groups such as formyloxy, acetyloxy, pivaloyloxy,

benzoyloxy and p-methoxyphenylcarbonyloxy.

The carbamoyloxy groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> carbamoyloxy groups such as N,N-dimethylcarbamoyloxy, N,N-diethylcarbamoyloxy, morpholinocarbonyloxy, and N-n-octylcarbamoyloxy.

The alkoxy carbonyloxy groups include C<sub>2-10</sub>, preferably C<sub>2-6</sub> alkoxy carbonyloxy groups such as methoxycarbonyloxy, ethoxycarbonyloxy, t-butoxycarbonyloxy and n-octyloxycarbonyloxy.

The aryloxycarbonyloxy groups include C<sub>7-12</sub>, preferably C<sub>7-10</sub> aryloxycarbonyloxy groups such as phenoxy carbonyloxy and p-methoxyphenoxy carbonyloxy.

The alkylamino groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> alkylamino groups such as methylamino and dimethylamino.

The arylamino groups include C<sub>6-12</sub>, preferably C<sub>6-8</sub> arylamino groups such as anilino, N-methylanilino and diphenylamino).

The heterocyclic amino groups include C<sub>1-12</sub>, preferably C<sub>2-6</sub> heterocyclic amino groups such as imidazol-2-ylamino and pyrazol-3-ylamino.

The acylamino groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> alkylcarbonylamino groups such as formylamino, acetylamino and pivaloylamino, C<sub>6-12</sub>, preferably C<sub>6-8</sub> arylcarbonylamino groups such as benzoylamino, C<sub>2-12</sub>, preferably C<sub>2-6</sub> heterocyclic carbonylamino groups such as pyridine-4-

carbonylamino, thiophene-2-carbonylamino and morpholinocarbonylamino, and C<sub>2-10</sub>, preferably C<sub>4-8</sub> imido groups such as N-succinimido and N-phthalimido.

5 The ureido groups include C<sub>1-12</sub>, preferably C<sub>1-6</sub> ureido groups such as carbamoylamino, N,N-dimethylureido and N,N-diethylureido.

10 The alkoxy carbonylamino groups include C<sub>2-10</sub>, preferably C<sub>2-6</sub> alkoxy carbonylamino groups such as methoxycarbonylamino, ethoxycarbonylamino and t-butoxycarbonylamino.

15 The aryloxy carbonylamino groups include C<sub>7-12</sub>, preferably C<sub>7-9</sub> aryloxy carbonylamino groups such as phenoxy carbonylamino, p-chlorophenoxy carbonylamino and 4-methoxyphenoxy carbonylamino.

20 The sulfamoylamino groups include C<sub>0-10</sub>, preferably C<sub>0-6</sub> sulfamoylamino groups such as sulfamoylamino, N,N-dimethylaminosulfonylamino and N-(2-hydroxyethyl)sulfamoylamino.

25 The alkylsulfonylamino groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> alkylsulfonylamino groups such as methylsulfonylamino and butylsulfonylamino.

The arylsulfonylamino groups include C<sub>6-12</sub>, preferably C<sub>6-8</sub> arylsulfonylamino groups such as phenylsulfonylamino, 2,3,5-trichlorophenylsulfonylamino and p-methylphenylsulfonylamino.

The alkylthio groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> alkylthio groups such as methylthio, ethylthio and butylthio.

5 The arylthio groups include C<sub>6-12</sub>, preferably C<sub>6-8</sub> arylthio groups such as phenylthio, p-chlorophenylthio and m-methoxyphenylthio.

The heterocyclic thio groups include C<sub>2-10</sub>, preferably C<sub>2-6</sub> heterocyclic thio groups such as 2-benzothiazolylthio and 1-phenyltetrazol-5-ylthio.

10 The sulfamoyl groups include C<sub>0-10</sub>, preferably C<sub>0-6</sub> sulfamoyl groups such as sulfamoyl, N-ethylsulfamoyl, N,N-dimethylsulfamoyl, N-acetylsulfamoyl and N-benzoylsulfamoyl.

15 The alkylsulfinyl groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> alkylsulfinyl groups such as methylsulfinyl and ethylsulfinyl.

The arylsulfinyl groups include C<sub>6-12</sub>, preferably C<sub>6-8</sub> arylsulfinyl groups such as phenylsulfinyl and p-methylphenylsulfinyl.

20 The alkylsulfonyl groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> alkylsulfonyl groups such as methylsulfonyl and ethylsulfonyl.

The arylsulfonyl groups include C<sub>6-12</sub>, preferably C<sub>6-8</sub> arylsulfonyl groups such as phenylsulfonyl and p-chlorophenylsulfonyl.

25 The acyl groups include formyl group, C<sub>2-10</sub>,

preferably C<sub>2-6</sub> alkylcarbonyl groups such as acetyl, pivaloyl and 2-chloroacetyl, and C<sub>7-12</sub>, preferably C<sub>7-9</sub> arylcarbonyl groups such as benzoyl and 2,4-dichlorobenzoyl.

5           The alkoxy carbonyl groups include C<sub>2-10</sub>, preferably C<sub>2-6</sub> alkoxy carbonyl groups such as methoxycarbonyl, ethoxycarbonyl, t-butoxycarbonyl and isobutoxycarbonyl.

10           The aryloxy carbonyl groups include C<sub>7-12</sub>, preferably C<sub>7-9</sub> aryloxy carbonyl groups such as phenoxy carbonyl, 2-chlorophenoxy carbonyl, 3-nitrophenoxy carbonyl and 4-t-butylphenoxy carbonyl.

15           The carbamoyl groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> carbamoyl groups such as carbamoyl, N-methylcarbamoyl, N,N-dimethylcarbamoyl, N-(2-hydroxyethyl)carbamoyl and N-(methylsulfonyl)carbamoyl.

20           The arylazo groups include C<sub>6-12</sub>, preferably C<sub>6-8</sub> arylazo groups such as phenylazo and p-chlorophenylazo.

25           The heterocyclic azo groups include C<sub>1-10</sub>, preferably C<sub>1-6</sub> heterocyclic azo groups such as pyrazol-3-ylazo, thiazol-2-ylazo, 5-ethylthio-1,3,4-thiadiazol-2-ylazo.

30           The phosphino groups include C<sub>2-12</sub>, preferably C<sub>2-6</sub> phosphino groups such as dimethylphosphino, diphenylphosphino and methylphenoxyphosphino.

35           The phosphinyl groups include C<sub>2-12</sub>, preferably C<sub>2-6</sub> phosphinyl groups such as phosphinyl and diethoxyphosphinyl.

40           The phosphinyloxy groups include C<sub>2-12</sub>, preferably C<sub>2-6</sub>

phosphinyloxy groups such as diphenoxypyrophosphinyloxy and dibutoxypyrophosphinyloxy.

The phosphinylamino groups include  $C_{2-12}$ , preferably  $C_{2-6}$  phosphinylamino groups such as dimethoxyphosphinylamino and dimethylaminophosphinylamino.

5 The silyl groups include  $C_{3-12}$ , preferably  $C_{3-8}$  silyl groups such as trimethylsilyl, t-butyldimethylsilyl and phenyldimethylsilyl.

10 When the above-described substituents  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are further substitutable, they may have one or more substituents. In such a case, preferable substituents are the same substituent groups as described above and a preferable range of the total number of the carbon atoms of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  does not exceed the above-described range.

15 When they have two or more substituents, the substituents may be the same or different.

20 In  $-NHSO_2R^5$  represented by X in formula (1), the preferable number of carbon atoms of the alkyl group, aryl group or heterocyclic group represented by  $R^5$  and specific examples of the group are the same as those described above in the substituents represented by  $R^1$  to  $R^4$ .

25 In the group represented by A, that is, a group represented by any one of formulas (Cp-1) through (Cp-12) in formula (1), the preferable number of carbon atoms of the group represented by  $R^{11}$  to  $R^{39}$  and  $R^{101}$  to  $R^{103}$  and

specific examples of the group are the same as those described above in the substituents represented by  $R^1$  to  $R^4$ , with the proviso that at least one of  $R^{102}$  and  $R^{103}$  is an electron attractive group having a Hammett  $\sigma_p$  value of 0.1 or greater, preferably 0.2 or greater. Examples of the 5 electron attractive group having a Hammett  $\sigma_p$  value of 0.1 or greater include a chlorine, bromine or iodine atom, or an alkoxy carbonyl, carbamoyl, alkylaminocarbonyl, dialkylaminocarbonyl, sulfamoyl, alkylaminosulfonyl, dialkylaminosulfonyl or acyl group. The Hammett empirical 10 rule was advocated by L.P. Hammett in 1935 in order to quantitatively discuss the influence of a substituent on the reaction or equilibrium of a benzene derivative and its validity is now recognized widely. The substituent 15 constants determined by the Hammett rule are  $\sigma_p$  and  $\sigma_m$  values. These values are found generally in many books and described in detail, for example, in *Lange's Handbook of Chemistry*, 12 ed., 1979, ed. J.A. Dean, (published by McGraw-Hill), *Journal of Japanese Chemistry*, Extra Number, 20 122, 96-103(1979) (published by Nankodo) and *Chemical Review*, 91, 165-195(1991).

The preferable range of dissociative direct dye (1) will next be described.

As  $R^1$  or  $R^2$  in formula (1), preferred are a hydrogen 25 atom, halogen atoms, alkyl groups, a cyano group, acylamino

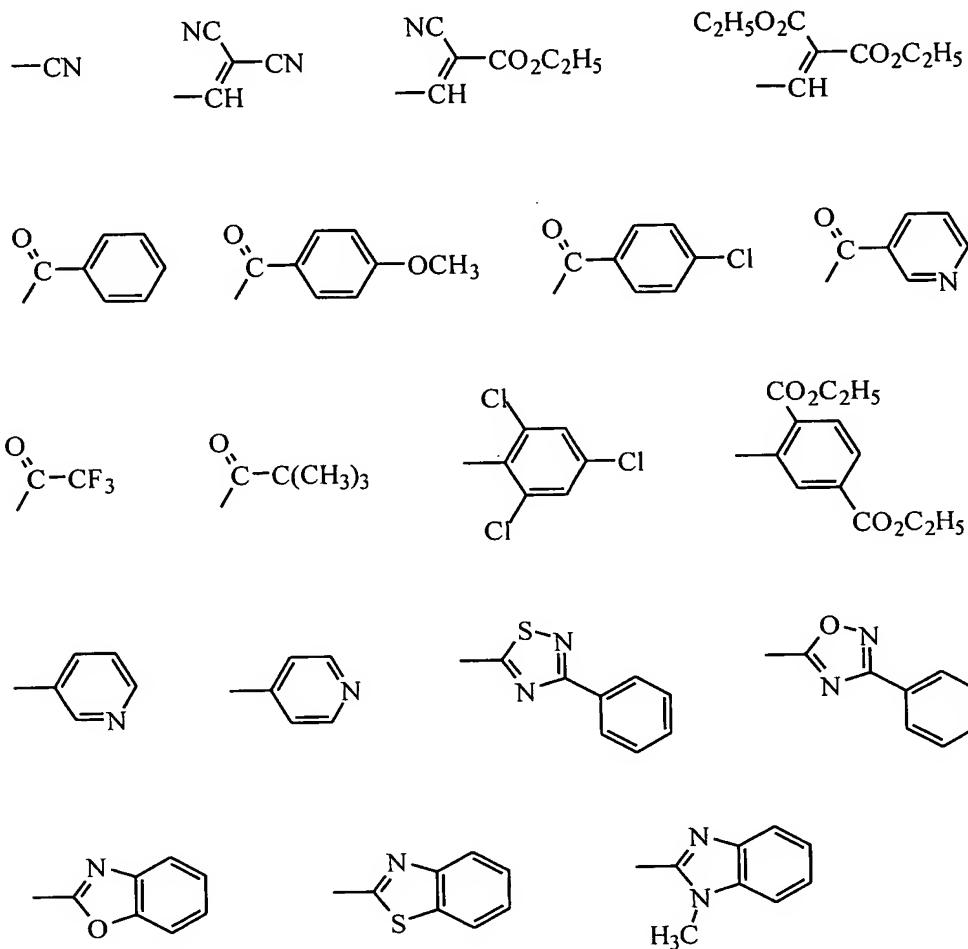
groups, ureido groups, alkoxy carbonylamino groups, aryloxycarbonylamino groups, sulfamoylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups, alkoxy carbonyl groups, sulfamoyl groups and carbamoyl groups, of which a hydrogen atom, a chlorine atom, a bromine atom, alkyl groups, a cyano group, acylamino groups, ureido groups, alkoxy carbonylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups and carbamoyl groups are more preferred, with hydrogen and chlorine atoms and acylamino and carbamoyl groups being most preferred.

As  $R^3$  or  $R^4$  in formula (1), preferred are a hydrogen atom, halogen atoms, alkyl groups and acylamino groups, of which a hydrogen atom, chlorine atom and alkyl groups are more preferred, with a hydrogen atom being most preferred.

As  $X$  in formula (1), a hydroxyl group is more preferred. When  $X$  represents  $-NHSO_2R^5$ ,  $R^5$  preferably represents an alkyl group.

As  $A$  in formula (1), the below-described groups are preferred.

In formula (Cp-1), preferred as  $R^{11}$  are a cyano group, acyl groups, heterocyclic groups and  $-C(R^{101})=C(R^{102})-R^{103}$ , with the following groups being particularly preferred.



In formula (Cp-2), preferred as  $\text{R}^{12}$  are a cyano group, aryl groups and heterocyclic groups. The cyano group and heterocyclic groups exemplified above as particularly preferred specific examples as  $\text{R}^{11}$  are also preferred as  $\text{R}^{12}$ .  
 5      As  $\text{R}^{13}$  and  $\text{R}^{14}$ , a hydrogen atom, alkyl groups and aryl groups are preferred. It is preferred that at least one of  $\text{R}^{13}$  and  $\text{R}^{14}$  represents a hydrogen atom.

In formula (Cp-3), preferred as  $\text{R}^{15}$  are alkyl groups, amino group, alkylamino groups, arylamino groups, heterocyclic amino groups, alkoxy groups, acylamino groups,  
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alkoxycarbonylamino groups, ureido group, alkoxycarbonyl groups, carbamoyl groups and a cyano group, of which alkyl groups, acylamino groups, alkoxycarbonyl groups and a cyano group are more preferred. As R<sup>16</sup>, aryl groups and heterocyclic groups are preferred, with aryl groups being most preferred.

5 In formula (Cp-4), preferred as R<sup>17</sup> and R<sup>18</sup> are alkyl groups and aryl groups.

10 In formula (Cp-5), preferred as R<sup>19</sup> and R<sup>20</sup> are aryl groups and heterocyclic groups, with aryl groups being most preferred.

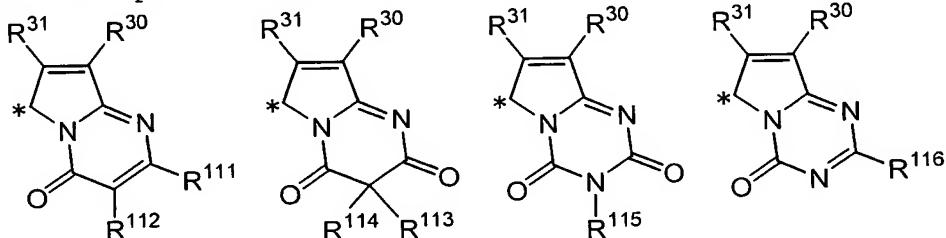
15 In formula (Cp-6), preferred as R<sup>21</sup> and R<sup>22</sup> are a cyano group, carbamoyl groups and alkoxycarbonyl groups, of which a cyano group and alkoxycarbonyl groups are more preferred. As R<sup>23</sup>, a hydrogen atom and alkyl groups are preferred.

20 In formula (Cp-7), preferred as R<sup>24</sup> are hydrogen atom, aryl groups, acylamino groups, alkylsulfonylamino groups and arylsulfonylamino groups. As R<sup>25</sup> and R<sup>26</sup>, a hydrogen atom, aryl groups, alkoxycarbonyl groups, carbamoyl groups, alkylsulfonyl groups, arylsulfonyl groups and a cyano group are preferred, with aryl groups, alkoxycarbonyl groups, carbamoyl groups and a cyano group being more preferred.

25 In formula (Cp-8), preferred as R<sup>27</sup> and R<sup>28</sup> are a cyano group, carbamoyl groups and alkoxycarbonyl groups,

while as  $R^{29}$ , halogen atoms, acylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups, alkoxycarbonyl groups, carbamoyl groups, alkylsulfonyl groups and arylsulfonyl groups are preferred. As  $s$ , an integer of from 0 to 2 is preferred.

In formula (Cp-9), preferred as  $R^{30}$  and  $R^{31}$  are a hydrogen atom, alkyl groups, aryl groups, heterocyclic groups, alkoxycarbonyl groups, carbamoyl groups, alkylsulfonyl groups, arylsulfonyl groups and a cyano group, of which alkyl groups, aryl groups, alkoxycarbonyl groups, carbamoyl groups and a cyano group are more preferred. As  $Z^1$ , groups capable of forming the below-described ring systems are preferred.

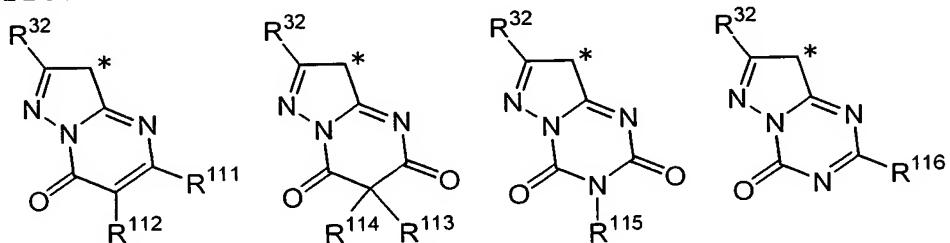


wherein,  $R^{111}$  represents a hydrogen atom or an alkoxy, amino, alkylamino, arylamino, heterocyclic amino, acylamino, ureido, alkoxycarbonylamino, aryloxycarbonylamino, sulfamoylamino, alkylsulfonylamino, arylsulfonylamino, alkylthio, arylthio or heterocyclic thio group,  $R^{112}$  represents a hydrogen or halogen atom, or an alkyl, acyl, carbamoyl or alkoxycarbonyl group,  $R^{113}$  and  $R^{114}$  each independently represents a hydrogen atom or an alkyl group,

5       $R^{115}$  represents a hydrogen atom or an alkyl group, and  $R^{116}$  represents a hydrogen atom or an alkyl, aryl, alkoxy, aryloxy, amino, alkylamino, arylamino, heterocyclic amino, acylamino, ureido, alkoxycarbonylamino, alkylsulfonylamino, arylsulfonylamino, alkylthio or arylthio group.

10     The preferable number of the carbon atoms of  $R^{111}$  to  $R^{116}$  and specific examples thereof are similar to those described above for the substituents represented by  $R^1$  to  $R^4$ .

15     In formula (Cp-10), preferred as  $R^{32}$  are hydrogen atom, alkyl groups, aryl groups, heterocyclic groups, alkoxycarbonyl groups, carbamoyl groups, alkylsulfonyl groups, arylsulfonyl groups and a cyano group, of which alkyl groups, aryl groups, alkoxycarbonyl groups, carbamoyl groups and a cyano group are more preferred. As  $Z^2$ , groups capable of forming the below-described ring systems are preferred.



20     wherein,  $R^{111}$  to  $R^{116}$  have the same meanings as described above.

    In formula (Cp-11),  $Z^3$  preferably represents  $-C(R^{36})=$ , and preferred are the case where  $R^{36}$  is a hydrogen

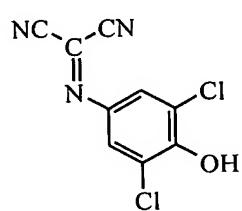
atom or an acylamino group,  $R^{33}$  and  $R^{34}$  each represents a hydrogen atom, a halogen atom, an alkyl group or acylamino group, and  $R^{35}$  represents a hydrogen atom or an alkyl group, and the case where  $R^{34}$  and  $R^{36}$  are coupled together to form 5 a benzene ring which may be substituted with a halogen atom or an amino, alkylamino, arylamino, heterocyclic amino, acylamino, ureido, alkoxy carbonylamino, alkylsulfonylamino or arylsulfonylamino group,  $R^{33}$  represents an acylamino, alkylsulfonylamino, arylsulfonylamino, carbamoylamino or 10 sulfamoyl group, and  $R^{35}$  represents a hydrogen atom.

In formula (Cp-12), preferred as  $R^{37}$  and  $R^{38}$  are a cyano group and alkoxy carbonyl groups, preferred as  $R^{39}$  are 15 halogen atoms, acylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups, alkoxy carbonyl groups, carbamoyl groups, alkylsulfonyl groups and arylsulfonyl groups, preferred as  $u$  is an integer of from 0 to 2, and preferred as  $Z^4$  is  $-SO_2-$ .

Among the dissociative direct dyes (1), those having 20 as A the group of formula (Cp-1), (Cp-2), (Cp-3), (Cp-4), (Cp-7), (Cp-9) or (Cp-11) are more preferred, of which those having as A the group of formula (Cp-1), (Cp-2), (Cp-3) or (Cp-11) are particularly preferred.

Preferable specific examples of the dissociative direct dye (1) will be shown below.

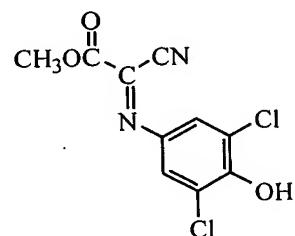
D-1



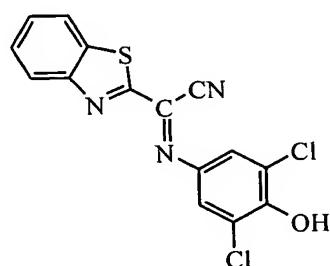
D-2



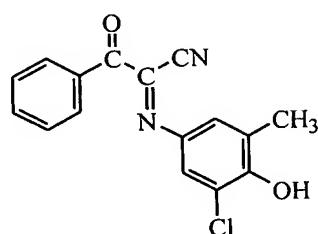
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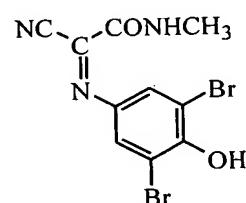
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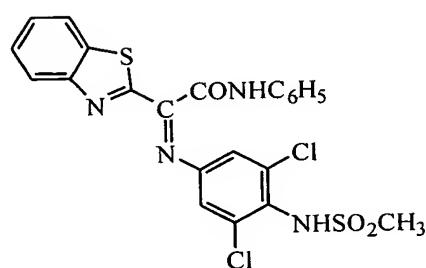
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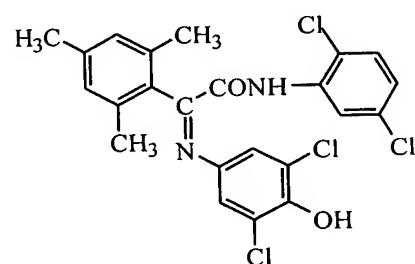
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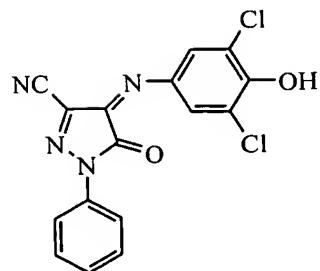
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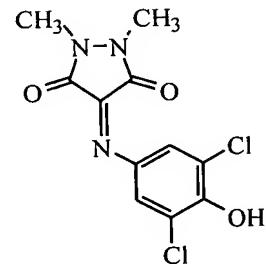
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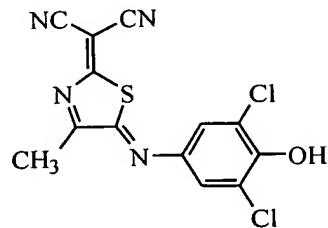
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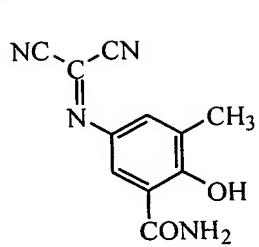
D-10



D-11



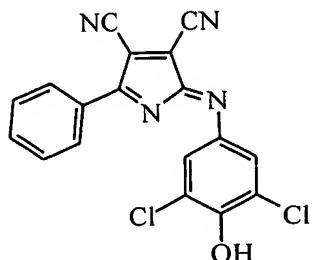
D-12



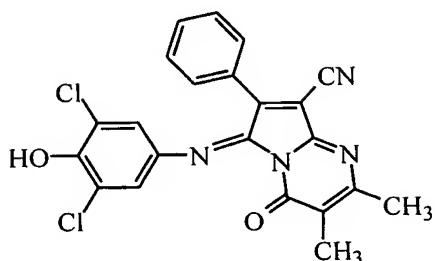
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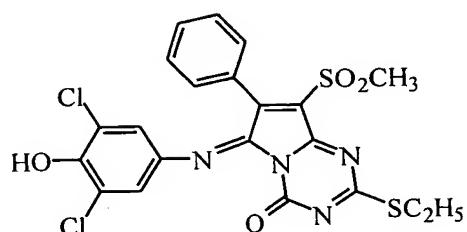
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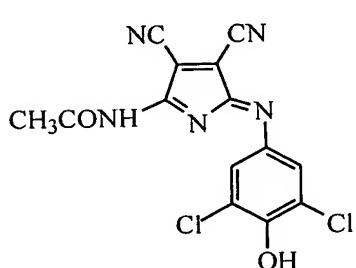
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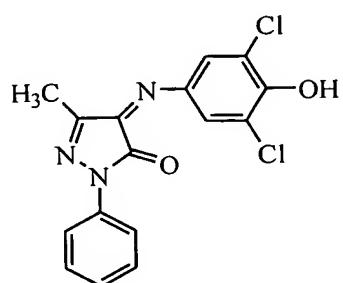
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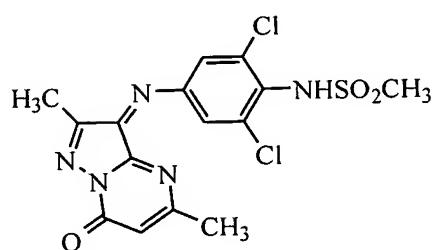
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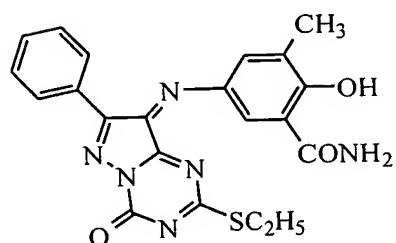
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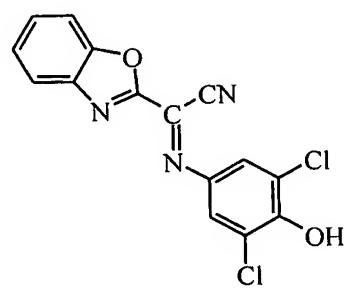
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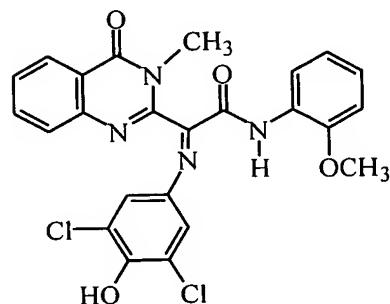
D-20



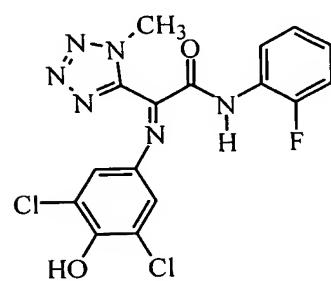
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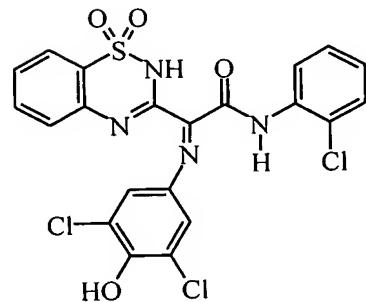
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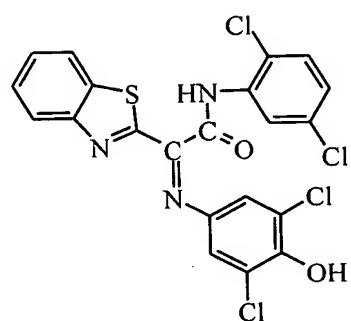
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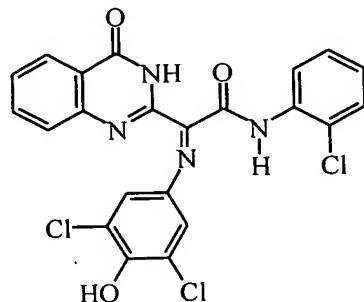
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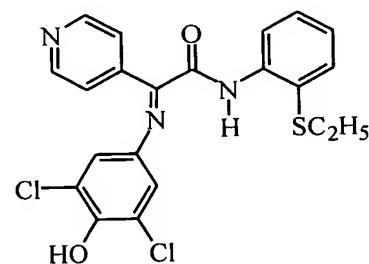
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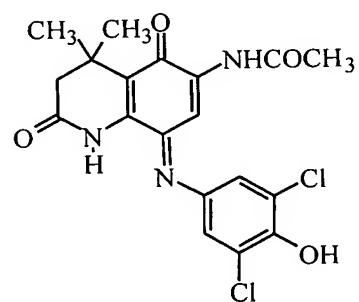
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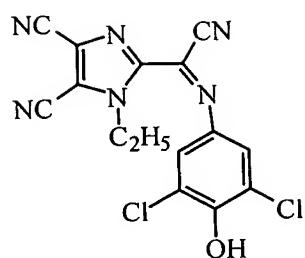
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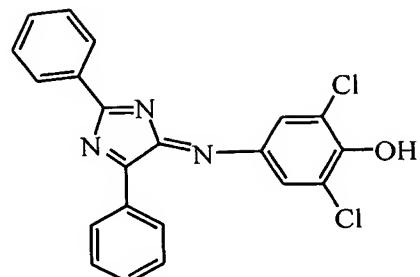
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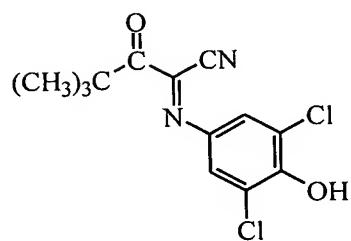
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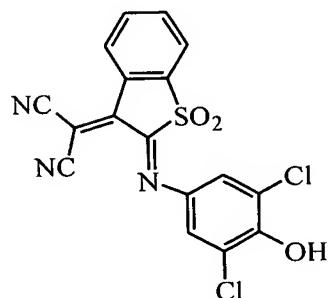
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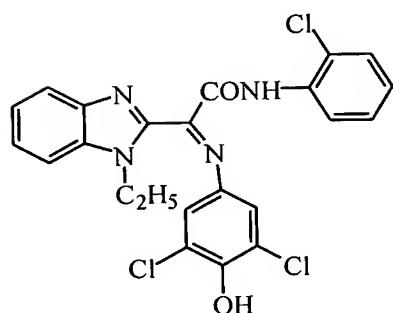
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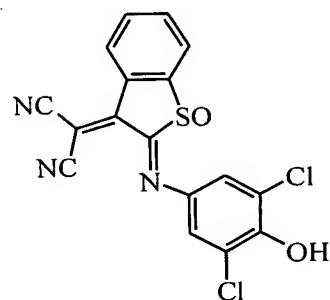
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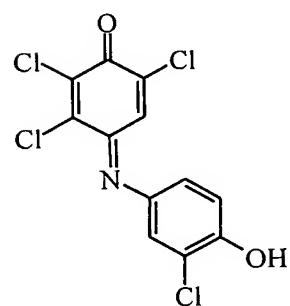
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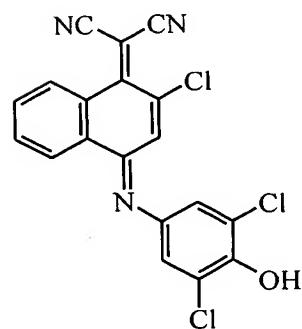
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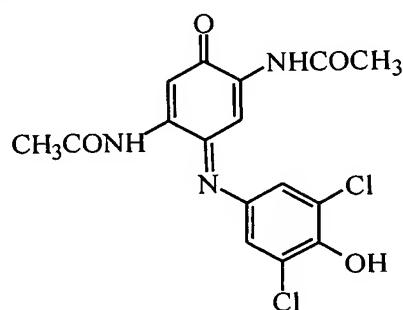
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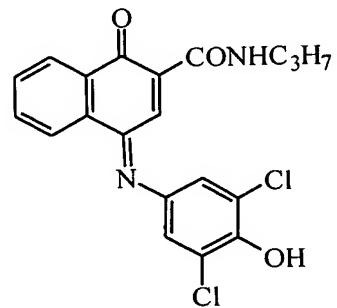
D-36



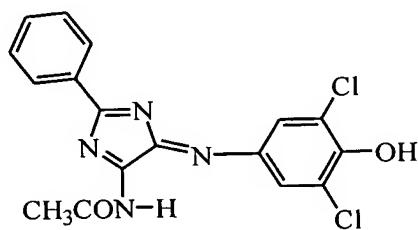
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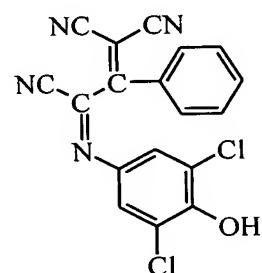
D-38



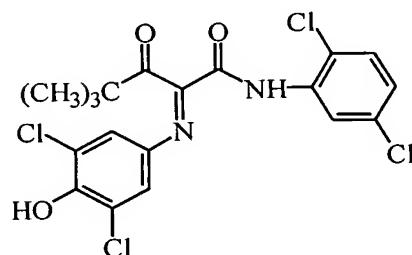
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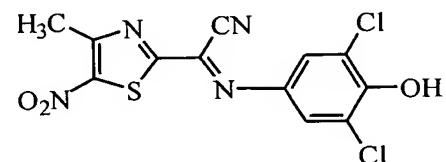
D-40



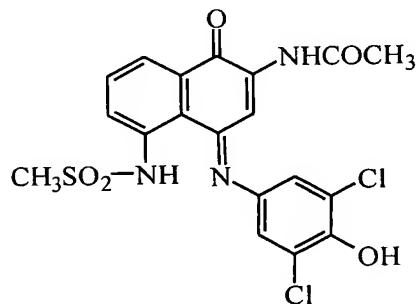
D-41



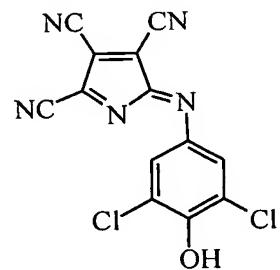
D-42



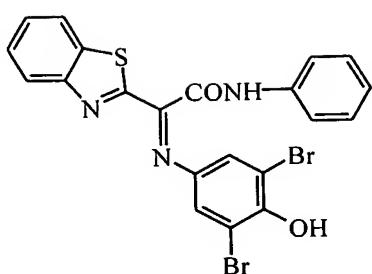
D-43



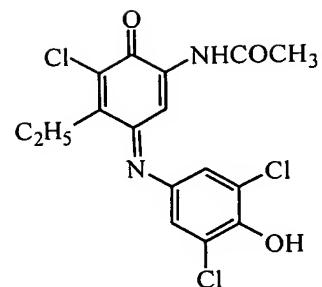
D-44



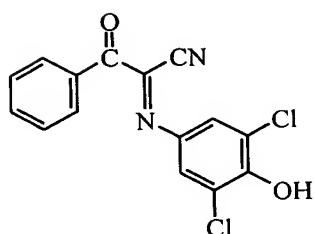
D-45



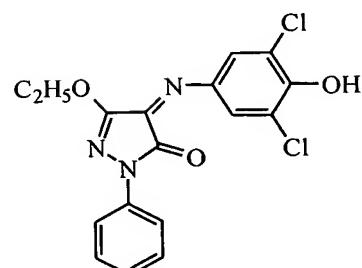
D-46



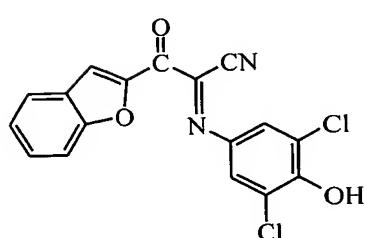
D-47



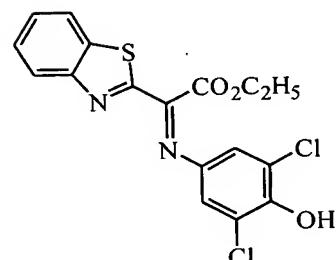
D-48



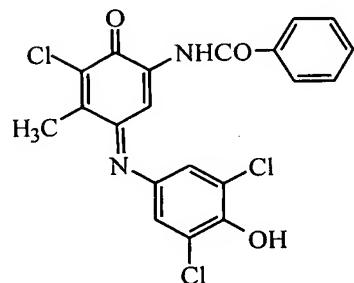
D-48



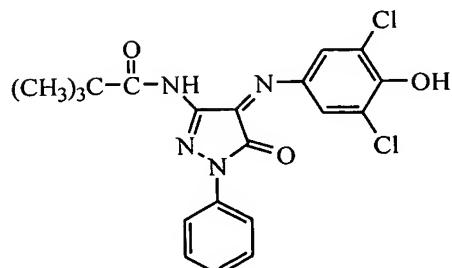
D-49



D-50



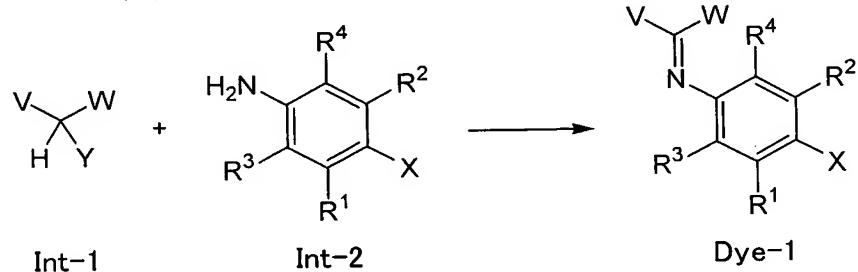
D-51



The dissociative direct dye (1) may be a salt of an

5        organic or inorganic acid, or a salt of an organic or inorganic alkali. Examples of the organic or inorganic acid include hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, propionic acid, lactic acid and citric acid, while those of the organic or inorganic alkali include ammonium hydroxide, 2-ethanolammonium hydroxide, sodium hydroxide and potassium hydroxide.

10      The dissociative direct dye (1) can be synthesized in accordance with the below-described reaction scheme. Specifically, Dye-1, which is a dissociative direct dye (1), is available by condensing Int-1 (wherein, Y represents a hydrogen atom, a halogen atom or a group capable of being dissociated as an anion) which is a coupler compound and Int-2, which is a p-aminophenol (or p-sulfonamidoaniline) derivative, in the presence of a base and an oxidizing agent. In the below-described scheme, V-C-W corresponds to A in formula (1).



20      A coupler compound such as Int-1 can be synthesized in accordance with a process as described in the literature on a coupler in the field of silver halide color photosensitive materials. Specifically, the process as

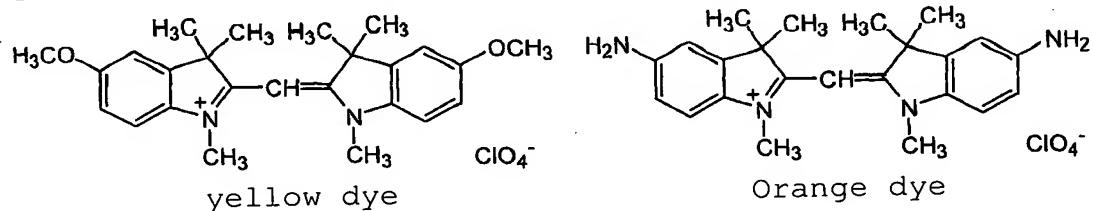
described in the literature cited on pp. 613 to 617 of Research Disclosure 40145 (September, 1997), or the process as described on pp. 80 to 83 of Research Disclosure 37038 (February, 1995) can be adopted.

5           The pKa of the dissociative direct dye (1) is preferably from 1.5 to 9, especially preferably from 2 to 8, most preferably from 2 to 7.5, from the viewpoint of hair coloring performance and color retention attained by the dye. The pKa value can be determined in the following 10 manner. First, a sample is dissolved in a 1:1 (volume ratio) solution of DMF and water to give its final concentration of  $2 \times 10^{-5}$  mol/L. After adjustment of the pH of the resulting solution to 2 with 1.0 mol/L hydrochloric acid, the solution was titrated with a 1.0 mol/L aqueous 15 solution of sodium hydroxide. Variations in a visible ultraviolet absorption spectrum is recorded and an inflection point is determined by regression analysis.

20           In the hair dye composition of the present invention, the dissociative direct dye (1) can be used in combination with another direct dye or an oxidation dye.

25           Examples of such a direct dye include Basic Blue 7 (C.I. 42595), Basic Blue 26 (C.I. 44045), Basic Blue 99 (C.I. 56059), Basic Violet 10 (C.I. 45170), Basic Violet 14 (C.I. 42515), Basic Brown 16 (C.I. 12250), Basic Brown 17 (C.I. 12251), Basic Red 2 (C.I. 50240), Basic Red 12 (C.I.

48070), Basic Red 22 (C.I. 11055), Basic Red 46 (C.I. 110825), Basic Red 76 (C.I. 12245), Basic Red 118 (C.I. 12251:1), Basic Yellow 28 (C.I. 48054) and Basic Yellow 57 (C.I. 12719); cationic dyes as described in Japanese Patent Laid-Open Nos. 2204/1983 and 118832/1997, and Japanese Language Laid-Open Publications (PCT) Nos. 501322/1996 and 507545/1996; and methine type cationic dyes having a cyanine structure represented by the following formulas:



10 The dissociative direct dye (1) is added preferably  
in an amount of 0.0001 to 20 wt.%, more preferably 0.001 to  
20 wt.%, more preferably from 0.05 to 10 wt.%, especially  
preferably from 0.1 to 5 wt.% based on the whole  
composition (after mixing of all the component parts when  
15 the composition is a two part or three part composition;  
this will be applied equally hereinafter). When another  
direct dye is used in combination, the total content of the  
dissociative direct dye (1) and the another direct dye  
preferably ranges from 0.001 to 20 wt.%, more preferably  
20 from 0.01 to 20 wt.%, still more preferably from 0.05 to 10  
wt.%, especially preferably from 0.1 to 5 wt.%.

In the hair dye composition of the present invention, the dissociative direct dye (1) exhibits a high storage

stability within a wide pH range from 2 to 11 which is a pH range employed ordinarily for hair dyes, so that the hair dye composition of the present invention can be used at any pH in the above-described pH range. Use in a pH range of 5 from 5 or greater is however preferred from the viewpoint of dyeing property. Moreover, owing to the high stability of the dissociative direct dye (1) against an alkali agent, the hair dye composition of the present invention can be used at a pH 8 or greater, particularly 8 to 11 which permits the composition to exhibit a high dyeing property, so that even after long storage, a high dyeing property can be kept without causing decomposition of the direct dye.

Examples of the alkali agent used for the hair dye composition of the present invention include ammonia, 15 alkanolamines such as monoethanolamine and isopropanolamine or salts thereof, guanidium salts such as guanidine carbonate, and hydroxides such as sodium hydroxide. The alkali agent is added preferably in an amount of from 0.01 to 20 wt.%, more preferably 0.1 to 10 wt.%, especially 20 preferably 0.5 to 5 wt.% based on the whole composition.

Since the dissociative direct dye (1) has a high stability against an oxidizing agent, it can be applied to the hair after mixing with an oxidizing agent. In other words, it can be provided as a two-part composition composed of a first part containing the dissociative direct

dye (1) and a second part containing an oxidizing agent.

In this case, hair dyeing and bleaching can be carried out simultaneously, which facilitates more vivid hair dyeing.

Examples of the oxidizing agent include hydrogen peroxide, persulfates such as ammonium persulfate, 5 potassium persulfate and sodium persulfate, perborates such as sodium perborate, percarbonates such as sodium percarbonate and bromates such as sodium bromate and potassium bromate. Hydrogen peroxide is especially preferred from the viewpoints of hair bleaching property, 10 stability and effectiveness of the dissociative direct dye (1). Hydrogen peroxide may be used in combination with another oxidizing agent. The oxidizing agent is added preferably in an amount of from 0.5 to 10 wt.%, especially 15 preferably from 1 to 8 wt.%, based on the whole composition.

The first part containing the dissociative direct dye (1) and the second part containing the oxidizing agent are mixed at a volume ratio preferably ranging from 2:1 to 1:3.

In the hair dye composition of the present invention, 20 an oxidation dye can be used in combination with the dissociative direct dye (1). Such combined use enables considerably vivid and intense dyeing which cannot be accomplished by the single use of the oxidation dye. For the oxidation dye, known developers and couplers ordinarily 25 employed for an oxidation type hair dye can be used.

Examples of the developer include paraphenylenediamine, toluene-2,5-diamine, 2-chloro-paraphenylenediamine, N-methoxyethyl-paraphenylenediamine, N,N-bis(2-hydroxyethyl)-paraphenylenediamine, 2-(2-hydroxyethyl)-paraphenylenediamine, 2,6-dimethyl-para-phenylenediamine, 4,4'-diaminodiphenylamine, 1,3-bis(N-(2-hydroxyethyl)-N-(4-aminophenyl)amino)-2-propanol, PEG-3,2,2'-paraphenylenediamine, paraaminophenol, paramethylaminophenol, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 2-(2-hydroxyethylaminomethyl)-4-aminophenol, orthoaminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-acetamidophenol, 3,4-diaminobenzoic acid, 5-aminosalicylic acid, 2,4,5,6-tetraaminopyrimidine, 2,5,6-triamino-4-hydroxypyrimidine and 4,5-diamino-1-(4'-chlorobenzyl)pyrazole and salts thereof.

Examples of the coupler include metaphenylenediamine, 2,4-diaminophenoxyethanol, 2-amino-4-(2-hydroxyethylamino)anisole, 2,4-diamino-5-methylphenetole, 2,4-diamino-5-(2-hydroxyethoxy)toluene, 2,4-dimethoxy-1,3-diaminobenzene, 2,6-bis(2-hydroxyethylamino)toluene, 2,4-diamino-5-fluorotoluene, 1,3-bis(2,4-diaminophenoxy)propane, metaaminophenol, 2-methyl-5-aminophenol, 2-methyl-5-(2-hydroxyethylamino)phenol, 2,4-dichloro-3-aminophenol, 2-chloro-3-amino-6-methylphenol, 2-methyl-4-chloro-5-

aminophenol, N-cyclopentyl-metaaminophenol, 2-methyl-4-methoxy-5-(2-hydroxyethylamino)phenol, 2-methyl-4-fluoro-5-aminophenol, resorcin, 2-methylresorcin, 4-chlororesorcin, 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-5 dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2-isopropyl-5-methylphenol, 4-hydroxyindole, 5-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole, 6-hydroxybenzomorpholine, 3,4-methylenedioxyphenol, 2-bromo-4,5-methylenedioxyphenol, 3,4-methylenedioxyaniline, 1-(2-hydroxyethyl)amino-3,4-10 methylenedioxybenzene, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-diaminopyridine, 2,3-diamino-6-methoxypyridine, 2-methylamino-3-amino-6-methoxypyridine, 2-amino-3-hydroxypyridine, and 2,6-diaminopyridine and salts thereof.

15 As each of the developer and coupler, at least two of the above-described developer or coupler are usable. The content of each of them is preferably from 0.01 to 20 wt.%, especially preferably from 0.5 to 10 wt.% based on the whole composition.

20 To the hair dye composition of the present invention, an autoxidation dye typified by an indole or an indoline, or a known direct dye such as a nitro dye or a disperse dye can also be added.

25 Addition of a polyol, polyol alkyl ether, cationic or amphoteric polymer or silicone to the hair dye composition

of the present invention is preferred, because the resulting composition can dye the hair uniformly and has improved cosmetic effects of the hair.

In addition to the above-described components, those ordinarily employed as a raw material for cosmetics can be added to the hair dye composition of the present invention. Examples of such an optional component include hydrocarbons, animal or vegetable fats and oils, higher fatty acids, organic solvents, penetration promoters, cationic surfactants, natural or synthetic polymers, higher alcohols, ethers, amphoteric surfactants, nonionic surfactants, anionic surfactants, protein derivatives, amino acids, antiseptics, chelating agents, stabilizers, antioxidants, plant extracts, crude drug extracts, vitamins, colorants, perfumes and ultraviolet absorbers.

The hair dye composition of the present invention can be prepared in a conventional manner to form a one-part composition, a two-part composition having a first part containing an alkali agent and a second part containing an oxidizing agent, or a three-part composition having, in addition to these two parts, a powdery oxidizing agent such as persulfate. The direct dye (1) may be incorporated in at least one of these parts of the two-part or three-part composition. The direct dye (1) may be incorporated in at least one of these parts of the two-part or three-part

composition. When the hair dye composition of the present invention is one-part type, it is applied to the hair directly, while when it is two- or three-part type, these parts are mixed upon hair dyeing and the mixture is applied 5 to the hair.

In the case of preparation of the hair dye composition of the present invention as a two-part type, the first part is typically prepared by mixing the dissociative direct dye (1) and optionally an oxidation dye 10 and adjusting the pH of the mixture to 8 to 12 with an alkali agent such as ammonia. The second part is prepared by incorporating about 2 to 6 wt.% of hydrogen peroxide, adjusting the mixture to weakly acidic with phosphoric acid. When the composition is a three-part type, a persulfate is 15 mixed with an inert substance such as talc or dextrin and a bonding agent to convert the mixture into a granular substance containing about 5 to 95 wt.% of persulfate. The granular substance is added to a mixture of the first part and the second part upon use.

20 The hair dye composition of the present invention can be provided in the form of powder, transparent liquid, emulsion, cream, gel, paste, aerosol, aerosol foam or the like. It preferably has a viscosity of 2000 to 100000 mPa·s upon its application to the hair (after mixing of all 25 the parts when the composition is a two-part or three-part

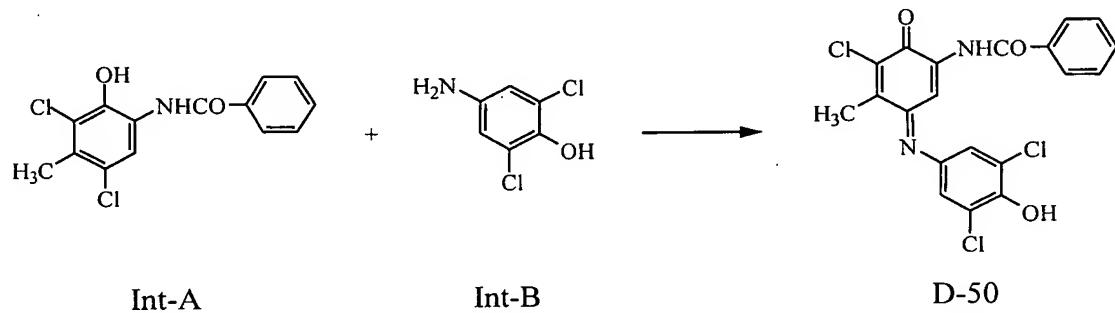
type). The above-described viscosity is measured at 20°C by using a Brookfield rotary viscometer (No. 5 spindle, 5 rpm).

### -Examples-

5 The synthesis examples of the dissociative direct dye  
(1) will next be described specifically.

Synthesis Example 1 <Synthesis of Exemplified Compound D-50>

Synthesis was conducted in accordance with the following scheme.

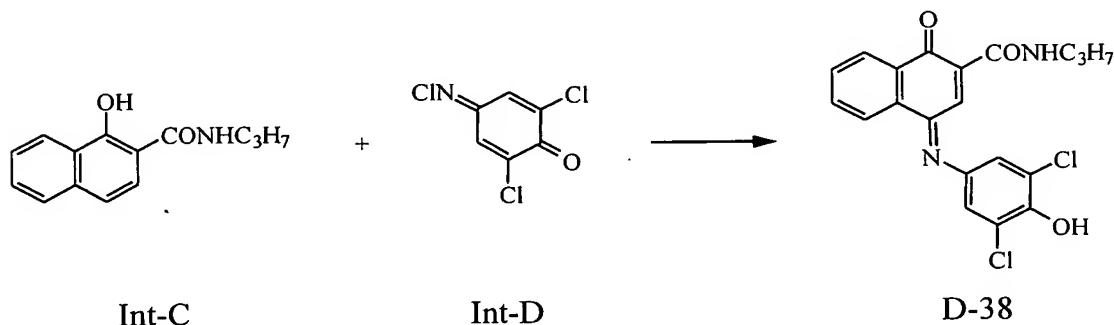


To 100 mL of ethyl acetate were added 2.96 g of N-(3,5-dichloro-2-hydroxy-4-methylphenyl)benzamide (Int-A), 2.10 g of commercially available 4-amino-2,6-dichlorophenol (Int-B), and 5.6 mL of triethylamine. The resulting mixture was stirred at room temperature. After addition of 3.5 g of silver acetate in several portions, stirring of the mixture was continued for 3 hours. The reaction mixture was filtered under reduced pressure. The cake on the Nutsche was added to 200 mL of acetone. The mixture was heated under reflux for 1 hour under stirring, followed

by hot filtration. To the filtrate was added 1 mL of concentrated hydrochloric acid and the mixture was concentrated under reduced pressure. To the residue were added acetonitrile and water to disperse the former in the latter. The crystals thus precipitated were collected by filtration. After washing while pouring water, the crystals thus obtained were air dried, whereby 2.47 g of Exemplified Compound D-50 was obtained as dark purple crystals (yield: 57%).

10      Synthesis Example 2 <Synthesis of Exemplified Compound D-  
38>

Synthesis was conducted in accordance with the following scheme.

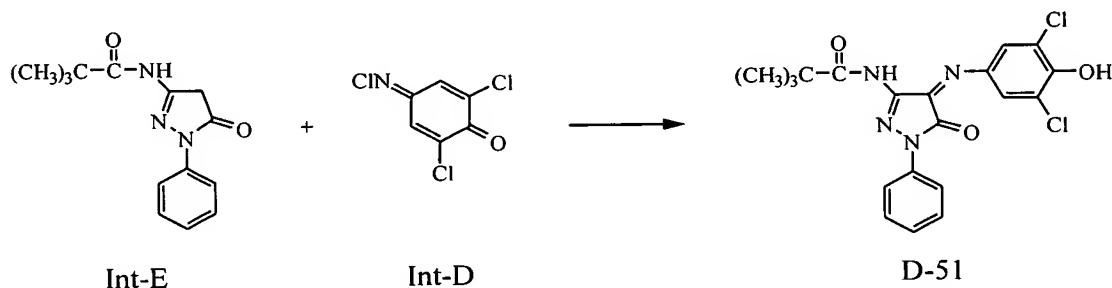


15 To 50 mL of ethyl acetate were added 2.37 g of N-  
propyl-1-hydroxy-2-naphthamide (Int-C) and 2.8 mL of  
triethylamine. The resulting mixture was stirred at room  
temperature. After addition of 2.20 g of commercially  
available 2,6-dichloroquinone-4-chloroimide (Int-D) in  
several portions, stirring was continued for 2 hours. To  
the reaction mixture were added 30 mL of acetonitrile and

dilute hydrochloric acid (obtained by diluting 1.9 mL of concentrated hydrochloric acid with 10 mL of water). The resulting mixture was stirred for 30 minutes. The crystals thus precipitated were filtered under reduced pressure and 5 then washed while pouring thereon 50 mL of water and then 20 mL of acetonitrile. The crystals were air dried, whereby 2.5 g of Exemplified D-38 was obtained as dark red crystals (yield: 62%).

Synthesis Example 3 <Synthesis of Exemplified Compound D-10 51>

Synthesis was conducted in accordance with the following scheme:

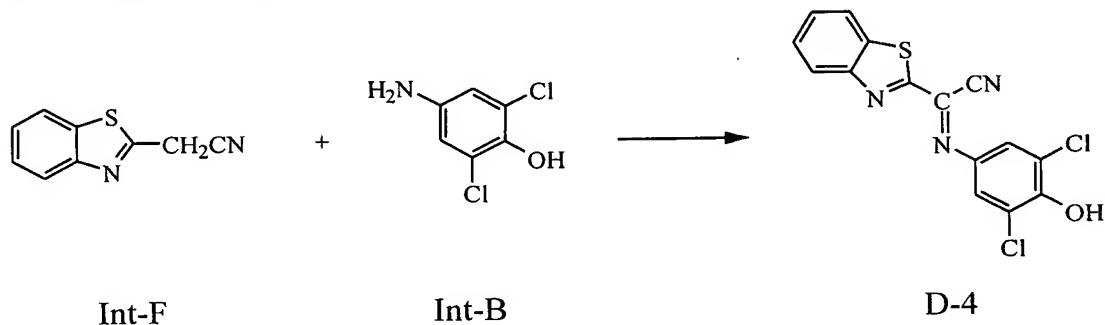


To 50 mL of ethyl acetate were added 2.59 g of N-(1-15 phenyl-5-pyrazol-3-yl)pivaloyl amide (Int-E) and 2.8 mL of triethylamine. The resulting mixture was stirred at room temperature. After addition of 2.20 g of commercially available 2,6-dichloroquinone-4-chloroimide (Int-D) in several portions, stirring was continued for 2 hours. The 20 reaction mixture was washed with dilute hydrochloric acid. The organic layer was washed with water twice, dried over

anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column (eluent: 2:1 mixed solvent of chloroform and ethyl acetate). The eluate was concentrated under reduced pressure. Acetonitrile (10 mL) was added to the residue to crystallize the same. The crystals thus precipitated were collected by filtration, washed while pouring a small amount of acetonitrile thereon, and air dried, whereby 0.44 g of Exemplified Compound D-51 was obtained as crystals (yield: 10%).

## Synthesis 4 <Synthesis of Exemplified Compound D-4>

Synthesis was conducted in accordance with the following scheme.



stirring was continued for 2 hours. The reaction mixture was filtered under reduced pressure. The cake on the Nutsche was added to 120 mL of water and the mixture was stirred at room temperature. Concentrated hydrochloric acid was added slowly to make the reaction mixture acidic (about pH 3 when measured by pH test paper). The crystals were collected by filtration and washed while pouring thereon 60 mL of water and then air dried, whereby 5.24 g of Exemplified Compound D-4 was obtained as yellowish brown crystals (yield: 75%).

Examples 1 to 4

Hair dye foams as shown in Table 1 were prepared in a manner known per se in the art.

Table 1

Component (wt.%)	Examples			
	1	2	3	4
Dye (D-50)	0.5	-	-	-
Dye (D-38)	-	0.5	-	-
Dye (D-51)	-	-	0.5	-
Dye (D-4)	-	-	-	0.5
Monoethanolamine	1	1	1	1
Ethanol	15	15	15	15
Propylene glycol	10	10	10	10
Polyoxyethylene (20) octyldecyl ether	10	10	10	10
Polyoxyethylene (9) tridecyl ether	3	3	3	3
Polyoxyethylene (3) tridecyl ether	6	6	6	6
Oleic diethanolamide	8	8	8	8
Oleyl alcohol	2	2	2	2
Ammonium chloride	q.s. *1	q.s. *1	q.s. *1	q.s. *1
LPG (4.0 kg/cm <sup>2</sup> )	10	11	12	12
Purified water	Balance	Balance	Balance	Balance

\*1: an amount to adjust the pH to 8.5

The above-described hair dye foams were each applied

to the goat hair at 30°C and was caused to act on the hair for 20 minutes. The hair thus dyed was then washed with an ordinarily used shampoo, followed by drying. As a result of the observation of the color tone of the dyed hair, it 5 exhibited good dyeing property and resistance to shampoo.

Examples 5 to 9

Two-part hair dyes as shown in Table 2 were prepared in a manner known per se in the art.

Table 2

Component (wt.%)		Examples				
		5	6	7	8	9
1-st part	Dye (D-50)	0.5	-	-	0.5	-
	Dye (D-38)	-	-	0.5	-	-
	Dye (D-51)	-	-	-	-	0.5
	Dye (D-4)	-	0.5	-	-	-
	HC Red 3	-	-	0.2	-	-
	p-Aminophenol	-	-	-	0.2	0.2
	p-Amino-o-cresol	-	-	-	0.2	0.2
	Ammonia (28 wt.%)	6	6	6	6	6
	Ethanol	15	15	-	-	-
	Propylene glycol	10	10	2	2	2
	Polyoxyethylene (20) octyldecyl ether	10	10	-	-	-
	Polyoxyethylene (40) cetyl ether	-	-	2	2	2
	Polyoxyethylene (2) cetyl ether	-	-	2.5	2.5	2.5
	Oleic diethanolamide	8	8	-	-	-
	Oleyl alcohol	2	2	-	-	-
	Stearyltrimethylammonium chloride	-	-	1.5	1.5	1.5
	Cetanol	-	-	1	1	1
	Liquid paraffin	-	-	0.5	0.5	0.5
2-nd part	Ammonium chloride	q.s.*2	q.s.*2	q.s.*2	q.s.*2	q.s.*2
	Sodium sulfite	-	-	-	0.5	0.5
	Tetrasodium edetate	0.1	0.1	0.1	0.1	0.1
	Purified water	Balance	Balance	Balance	Balance	Balance
2-nd part	Hydrogen peroxide	6	6	6	6	6
	Methyl paraben	0.1	0.1	0.1	0.1	0.1
	Phosphoric acid	q.s.*3	q.s.*3	q.s.*3	q.s.*3	q.s.*3
	Purified water	Balance	Balance	Balance	Balance	Balance

10 \*2: an amount to adjust the pH to 9.8.

\*3: an amount to adjust the pH to 3.5

After 1 part by weight of the first part was mixed with 1 part by weight of the second part, the resulting mixture was applied to the goat hair at 30°C and was caused to act on the hair for 20 minutes. The hair thus dyed was 5 then washed with an ordinarily used shampoo, followed by drying. As a result of the observation of the color tone of the dyed hair, it exhibited good dyeing property and resistance to shampoo.